Supplementary data for this paper are available from the IUCr electronic archives (Reference: OB1006). Services for accessing these data are described at the back of the journal.

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trans-(6-Bromo-2-cyclohexen-1-yl)-pyridinium bromide

Xinghua Han, Ronald J. Baker and John Masnovi

Department of Chemistry, Cleveland State University, Cleveland, OH 44115, USA. E-mail: j.masnovi@popmail.csuohio.edu

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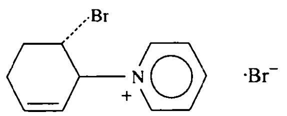
Abstract

The title compound, $C_{11}H_{13}BrN^{+}\cdot Br^{-}$, was prepared by bromination of 1,3-cyclohexadiene in the presence of stoichiometric amounts of bromine and pyridine. Bromine and pyridine are found to add by *anti* 1,2-addition, with pyridine occupying the allylic position. The bromide resides relatively close [3.490 (1) Å] to the covalent bromine, whereas it is 4.232 (5) Å from the nearest nitrogen cation.

Comment

Several reports concerning the structure of the products of bromination of 1,3-cyclohexadiene are in disagreement (Hassel & Lunde, 1950; Heasley *et al.*, 1973; Khedekar, 1997; McMillen & Grutzner, 1994; Lund, 1950). The first-formed dibromocyclohexenes are unstable liquids which undergo rearrangements at room temperature. Therefore, the bromination was conducted in the presence of pyridine at low temperature, and afforded the title compound, (I). Its structure was determined in order to establish the stereochemistry of addition of nucleophiles during the initial steps of bromination of 1,3-dienes. Because the nucleophile (pyridine) differs from the electrophile (bromine), the structure establishes the regiochemistry of the addition as well.



(I)

The structure shown in Fig. 1 demonstrates that the product is formed by *anti* 1,2-addition of the elements of bromine and pyridine across one of the double bonds of the diene. The pyridine attaches to the allylic-C atom. The pyridinium moiety is essentially planar and resembles that found in other *N*-alkylpyridinium derivatives (van Havere *et al.*, 1982), with relatively short (about 1.36 Å) carbon–carbon bonds and bond angles all near 120°. Bond distances and angles in the cyclohexene moiety are close to those in cyclohexene (Chiang & Bauer, 1969). For example, C1, C2, C3 and C4 are coplanar. Interior bond angles about the C=C double bond average 123.1° (123.5° in cyclohexene),

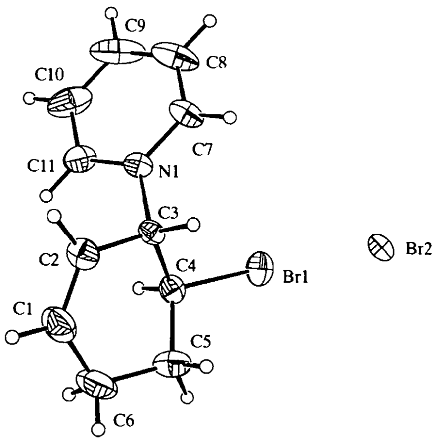


Fig. 1. *ORTEP*II (Johnson, 1976) representation showing the atom-numbering scheme with displacement ellipsoids at the 30% probability level.

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rather than the expected 120°, and bond distances between C atoms with sp^3 hybridization average 1.508 Å [being 1.515 (20) and 1.55 (4) Å in cyclohexene].

The cyclohexene ring adopts a half-chair conformation with the 4-bromine (Br1) equatorial. Interestingly, the bromide counter-ion closely approaches this bromine [3.490 (1) Å, with $\mathrm{Br}^-\cdots\mathrm{Br}$—C angle 164.7 (2)°]. This distance is about 0.3 Å smaller than a non-bonded contact expected between bromide and bromine, with radii about 1.95 and 1.85 Å, respectively (Huheey *et al.*, 1993; Shannon, 1976; Brock, 1980). Much larger distances [4.232 (5) and 4.414 (5) Å] are observed between the bromide and the two nearest nitrogen cations. Unfavorable steric interactions between the bromide and H atoms, as well as the covalent bromine, may inhibit closer approach between the bromide and the pyridinium nitrogen. Thus, H3, H4, H7 and H8 exhibit the closest non-bonded $\mathrm{Br}^-\cdots\mathrm{H}$ distances (less than 3 Å). The dihedral angle between the plane of the pyridine and the C6—C1—C2—C3 plane is 109. (4)° and the torsion angle C7—N1—C3—C2 is 133.9 (11)°. Thus approach to N1 is occluded by Br1, H4 and H2 above and below the plane of the pyridine ring, and by H3, H7 and H11 in the plane of the ring.

Experimental

The title compound was prepared by addition of one equivalent of bromine and one equivalent of pyridine to 1,3-cyclohexadiene in 1:1 *v*/*v* $\mathrm{CH_2Cl_2}$–$\mathrm{CCl_4}$ at 203 K. Crystals spontaneously deposited on standing, and were collected by filtration at room temperature.

Crystal data

$\mathrm{C_{11}H_{13}BrN^+\cdot Br^-}$
$M_r = 319.04$
Monoclinic
$P2_1/n$
$a = 6.9550\,(8)$ Å
$b = 14.4941\,(11)$ Å
$c = 12.2793\,(8)$ Å
$\beta = 101.523\,(7)°$
$V = 1212.88\,(18)$ Å^3
$Z = 4$
$D_x = 1.747$ Mg m^{-3}
D_m not measured

Mo $K\alpha$ radiation
$\lambda = 0.70930$ Å
Cell parameters from 25 reflections
$\theta = 6.0$–$12.0°$
$\mu = 6.65$ mm^{-1}
$T = 293$ K
Plate cut from long needle
0.42 × 0.24 × 0.14 mm
Colorless

Data collection

Nonius CAD-4 diffractometer
ω scans
Absorption correction: empirical (*ABSORP* in *NRCVAX*; Gabe *et al.*, 1989)
$T_{\min} = 0.182$, $T_{\max} = 0.394$
4585 measured reflections
2155 independent reflections

1494 reflections with $I_{\rm net} > 2\sigma(I_{\rm net})$
$R_{\rm int} = 0.074$
$\theta_{\max} = 25.02°$
$h = 0 \rightarrow -8$
$k = -17 \rightarrow 17$
$l = -14 \rightarrow 14$
3 standard reflections frequency: 120 min intensity decay: 3.4%

Refinement

Refinement on F
$R = 0.045$
$wR = 0.041$
$S = 1.78$
1492 reflections
127 parameters
H-atom parameters constrained

$w = 1/[\sigma^2(F) + 0.0002F^2]$
$(\Delta/\sigma)_{\max} < 0.001$
$\Delta\rho_{\max} = 0.72$ e Å^{-3}
$\Delta\rho_{\min} = -0.85$ e Å^{-3}
Extinction correction: none
Scattering factors from *International Tables for X-ray Crystallography* (Vol. IV)

Table 1. *Selected geometric parameters (Å, °)*

Br1—C4	1.936 (6)	C2—C3	1.495 (9)
N1—C3	1.500 (7)	C3—C4	1.512 (8)
C1—C2	1.320 (10)	C4—C5	1.508 (9)
C1—C6	1.459 (11)	C5—C6	1.503 (12)
C2—C1—C6	123.7 (7)	Br1—C4—C3	111.3 (4)
C1—C2—C3	122.5 (6)	Br1—C4—C5	110.7 (5)
N1—C3—C2	109.9 (5)	C3—C4—C5	110.6 (5)
N1—C3—C4	109.2 (4)	C4—C5—C6	109.5 (6)
C2—C3—C4	111.2 (5)	C1—C6—C5	113.3 (6)

H atoms were calculated at idealized positions and were refined with positional parameters and displacement coefficients riding on the C atoms to which they are attached, C—H 0.96 (alkene and pyridine), 0.98 (methylene) or 1.00 Å (methine). H atom U values were set 0.01 Å^2 larger than $U_{\rm iso}$ for the respective C atoms.

Data collection: *CAD-4-PC Software* (Enraf–Nonius, 1993). Cell refinement: *CAD-4-PC Software*. Data reduction: *DATRD*2 in *NRCVAX* (Gabe *et al.*, 1989). Program(s) used to solve structure: *SOLVER* in *NRCVAX*. Program(s) used to refine structure: *LSTSQ* in *NRCVAX*. Molecular graphics: *NRCVAX*. Software used to prepare material for publication: *TABLES* in *NRCVAX* (January 1994 version).

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